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14. ABSTRACT

There is a keen interest in understanding of the interaction between bio-molecules and nanostructured materials, due to the potential application of the unique signature of the latter in probing the structural and conformational changes of the former, possibly leading to new detection mechanisms. In this work, we investigated the electronic properties of carbon- and boron-based nanostructures with an aim to identify their role in the development of the next generation sensing devices. We find that

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Report Title

Fundamental Understanding of "Probe"-"Target" Molecular Interactions and Electronic Response for Nanoarchitecture-Based Real-Time Chemical and Biological Detection System.

"“Molecular Interactions & Electronic Response”

ABSTRACT

There is a keen interest in understanding of the interaction between bio-molecules and nanostructured materials, due to the potential application of the unique signature of the latter in probing the structural and conformational changes of the former, possibly leading to new detection mechanisms. In this work, we investigated the electronic properties of carbon- and boron-based nanostructures with an aim to identify their role in the development of the next generation sensing devices. We find that

(i) Single atom change in the structure can noticeably alter the properties the carbon fullerene system. Boron fullerenes and Graphene/BN bilayers also appear to be attractive candidates for future nanoscale electronics.

(ii) The interaction of DNA with BNNT depends upon the individual polarizability of biomolecules together with the degrees of mixing of electronic states with the tubular surface.

(iii) Noticeable changes in the conductivity of semiconducting BNNTs due to physisorption of nucleic acid base molecules are predicted. Guanine significantly enhances its conductivity by introducing conduction channels near the Fermi energy of the bioconjugated system. For metallic CNTs, a large background current masks relatively small changes in current due to the biomolecular adsorption. The results therefore suggest the suitability of BNNTs for biosensing applications.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

0

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Saikat Mukhopadhyay	0.50	
Xioaliang Zhong	0.50	
FTE Equivalent:	**1.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ravindra Pandey	0.30	
FTE Equivalent:	**0.30**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Saikat Mukhopadhyay
Xiaolaing Zhong
Total Number: 2

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

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Project Title: Fundamental Understanding of "Probe"-"Target" Molecular Interactions and Electronic Response for Nanoarchitecture-Based Real-Time Chemical and Biological Detection System.

Reporting Period: June 1, 2009 –December 31, 2012

"Molecular Interactions & Electronic Response"

Executive Summary

There is a keen interest in a thorough understanding of the interaction between bio-molecules and matter, especially nanostructured materials, due to the potential application of the unique signature of the latter in probing the structural and conformational changes of the former, possibly leading to new detection mechanisms. BNNTs offer an alternative to CNT based materials due to their chemical inertness and structural stability. In this work, we investigated the electronic properties of carbon- and boron-based nanostructures with an aim to identify their role in the development of the next generation electronic sensing devices. The calculated results based on density functional theory and non-equilibrium Green's function method find that

(i) Single atom change in the structure can noticeably alter the properties the carbon fullerene system. BC_{59} can be an effective semiconductor in p-type devices. Boron fullerenes and Graphene/BN bilayers also appear to be attractive candidates for future nanoscale electronics.

(ii) The interaction of DNA with BNNT depends upon the individual polarizability of biomolecules together with the degrees of mixing of electronic states with the tubular surface. On the other hand, sensitivity of BNNTs toward amino acid polarity is predicted a significantly higher compared to that of the CNTs.

(iii) Noticeable changes in the conductivity of semiconducting BNNTs due to physisorption of nucleic acid base molecules are predicted. Guanine significantly enhances its conductivity by introducing conduction channels near the Fermi energy of the bioconjugated system. For metallic CNTs, a large background current masks relatively small changes in current due to the biomolecular adsorption. The results therefore suggest the suitability of BNNTs for biosensing applications.

"Molecular Interactions & Electronic Response"

Statement of the problem studied

There is a keen interest in a thorough understanding of the interaction between bio-molecules and matter, especially nanostructured materials, due to the potential application of the unique signature of the latter in probing the structural and conformational changes of the former, possibly leading to new detection mechanisms. BNNTs offer an alternative to CNT based materials due to their chemical inertness and structural stability. Modulation of band gap of bioconjugated BNNTs may be useful in application of this class of biofunctional materials to the design of the next generation sensing devices. In this work, the electronic properties of carbon- and boron-based nanostructures were investigated with an aim to identify their role in the development of such sensing devices.

Our goals were:

(i) Investigate and understand electron transport properties of novel carbon and boron nanostructures.

(ii) Investigate molecular-level interactions of DNA and Amino Acids with Boron Nitride Nanotubes.

(iii) Investigate and understand electron transport properties of CNTs and BNNTs conjugated with biomolecules.

The studies on carbon and boron nanostructures (i.e. fullerenes and graphene/BN hybrid layers) were performed to benchmark the methodology and modeling elements for first principles electronic transport calculations on bioconjugated CNTs and BNNTs.

Summary of the most important results

(i) ***Electron transport properties of Boron doped fullerenes, Boron fullerenes and Graphene/BN hybrid systems:***

Boron doped fullerenes and Boron-fullerenes were investigated by first principles quantum mechanical methods for their stability and electron transport properties. The role of a single dopant atom in influencing the electronic response of the carbon fullerene system was examined. It was found that even a single atom change in the structure can noticeably alter the properties at nanoscale. BC_{59} exhibits a considerably higher magnitude of current, thus suggesting that it can be an effective semiconductor in p-type devices. The differential conductance and the tunnel current for B-fullerenes are calculated to be much larger than those for carbon fullerenes, making them to be attractive candidates for future nano-scale electronics.

The effect of electric field on the band structures of graphene/BN was examined. We predict that the modulation of band gap in graphene/BN bilayers is dominated by the features of graphene, and is related to the modification in molecular orbitals as revealed by the calculated projected density of states. The calculations also reveal that a bilayer graphene nanoribbons in the AA stacking configuration exhibit substantially enhanced electron transmission as well as tunneling currents. This feature of the bilayer graphene nanoribbons

can be exploited to develop practical devices, since it has been suggested that the application of bilayer GNRs in nanoscale devices is advantageous due to their low sensitivity to external perturbations.

(ii) ***Molecular-level Interaction of Nucleic Acid Bases and Amino Acids on Boron Nitride Nanotubes:***

First-principles quantum mechanical calculations were employed to study interaction of DNA with boron nitride nanotubes (BNNT). What distinguishes BNNTs from carbon nanotubes (CNTs) is the heterogeneous composition of the former. This chemical feature resulted in the observation that the binding energy of the base molecules not only depends upon their individual polarizability, but also marginally on the degrees of mixing of electronic states with the tubular surface of BNNT, leading to mid-gap states emerging in the conjugated system. The higher binding energy of the guanine-BNN conjugate and the associated smaller band gap relative to that of the pristine BNNT could potentially be very useful characteristics in applications for the design of next-generation sensing devices.

As proteins play one of the most important roles in biology, it is expected that a similar understanding of their interactions with nanomaterials, as for DNA, would provide critical fundamental knowledge on their interactions and possibly guide for utilizing nanotechnology in proteomics.

Next, the effect of molecular polarity on the interaction between BNNTs and amino acids was investigated. The polar molecules, Asp and Arg exhibit a relatively stronger binding with the tubular surface of BNNT (Figure 1). The binding between the polar amino acid molecules and BNNT is accompanied with a charge transfer from the former to the later, suggesting that stabilization of the bioconjugated complex is mainly governed by the electrostatic interactions (Figure 2). The results also predict modulation of the BNNT band gap by Trp. Interestingly, no change in the band gap of BNNT is seen by the polar molecules Asp and Arg. The predicted higher sensitivity of BNNTs compared to the carbon nanotubes (CNTs) toward amino acid polarity suggests the former to be a better substrate for protein immobilization than CNTs.

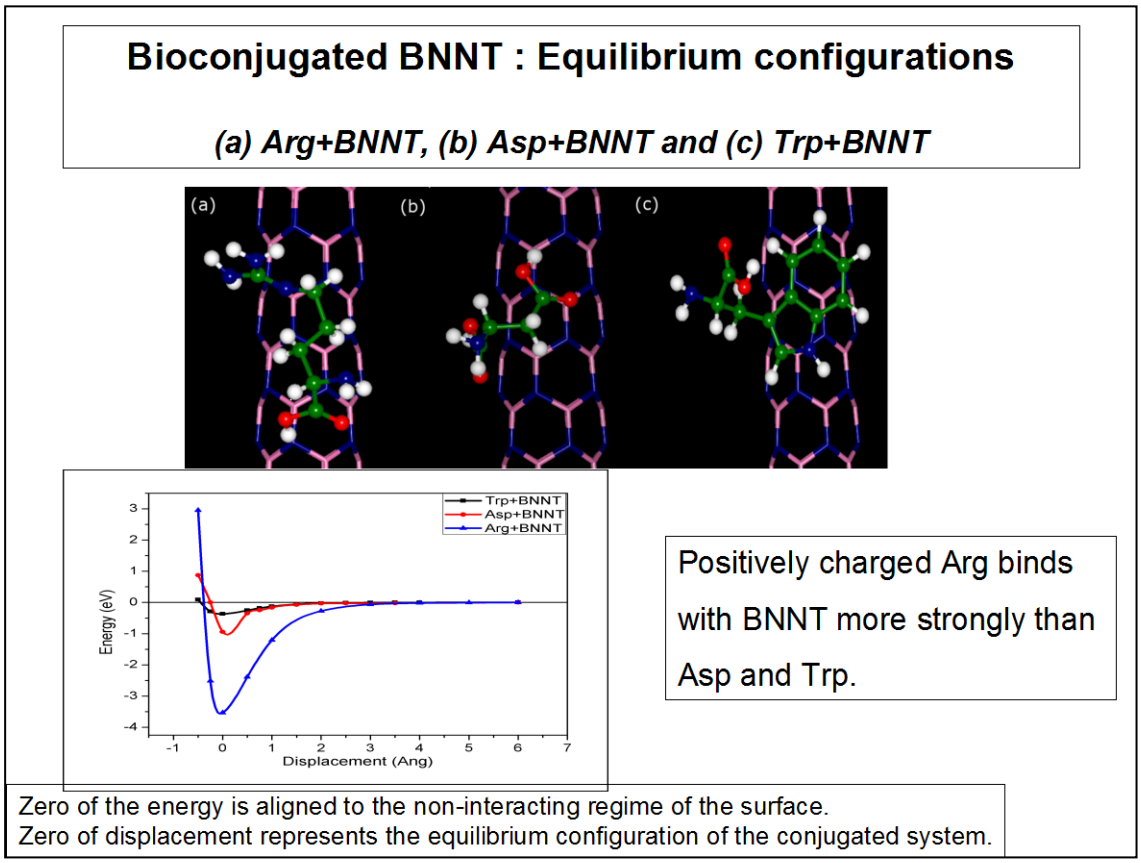


Figure 1: Bioconjugated BNNT: ground state configurations.

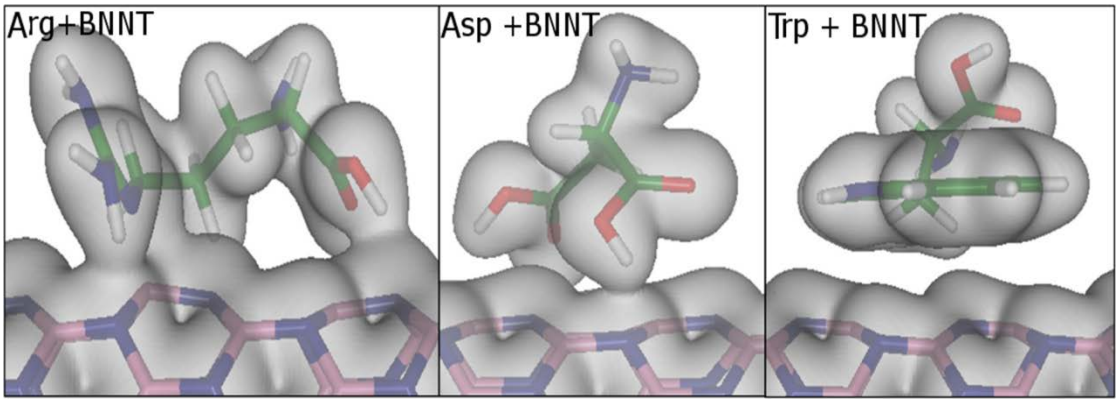


Figure 2: Bioconjugated BNNT: Charge Density

(iii) ***Electronic response of the bioconjugated CNTs and BNNTs:***

The electronic response of the DNA+CNT and DNA+BNNT conjugated systems was investigated via calculations of the I-V characteristics of the system (Figure 3).

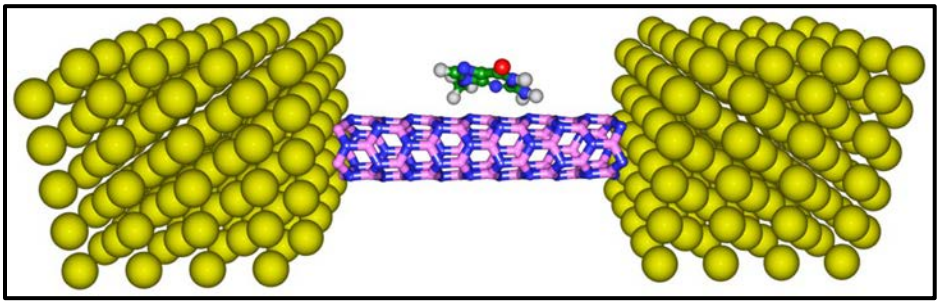


Figure 3. A schematic view of guanine + BNNT coupled with [110] gold electrodes. Symbols: Au in yellow, B in pink, N in blue, H in grey, C in green and O in red.

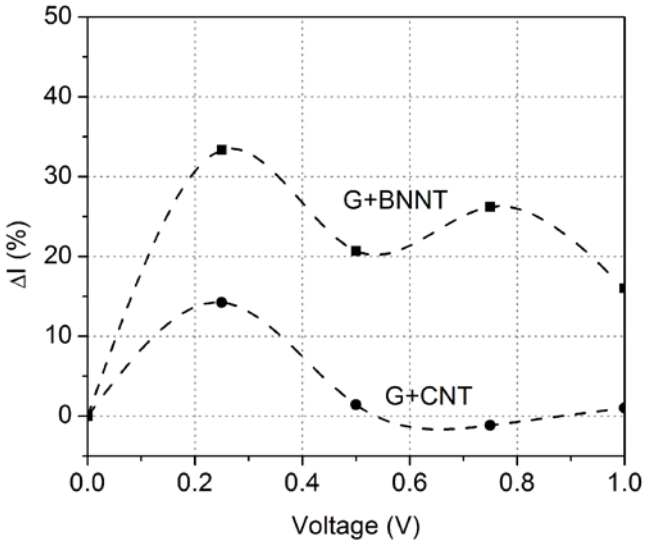


Figure 4. The normalized current ($\Delta I = (I_{NT+G}-I_{NT})/I_{NT}$) vs. bias voltage of the guanine conjugated complexes relative to that of the pristine nanotubes.

The calculated results predict noticeable changes in the conductivity of semiconducting BNNTs due to physisorption of nucleic acid base molecules. Specifically, guanine which binds to the side wall of BNNT significantly enhances its conductivity by introducing conduction channels near the Fermi energy of the bioconjugated system. For metallic CNTs, a large background current masks relatively small changes in current due to the biomolecular adsorption. The results therefore suggest the suitability of BNNTs for biosensing applications.

Papers Published in Peer-Review Journals:

Appl. Phys. Lett., in press, (2013)
X. Zhong, S. Mukhopadhyay, S. Gowtham, R. Pandey1 and S. P. Karna
"Applicability of carbon and boron nitride nanotubes as biosensors: Effect of biomolecular adsorption on the transport properties of carbon and boron nitride nanotubes."

Appl. Phys. Lett., 100, 52104 (2012)
R. Balu, X. Zhong, R. Pandey, S. P. Karna
"Effect of Electric Field on the Band Structure of Graphene/Boron Nitride and Boron Nitride/Boron Nitride Bilayers."

Carbon, 50, 784 (2012)
X. Zhong, R. Pandey, S. P. Karna
"Stacking Dependent Electronic Structure and Transport in Bilayer Graphene Nanoribbons."

J. Phys. Chem. Lett., 2, 2442 (2011)
S. Mukhopadhyay, R. H. Scheicher, R. Pandey, S. P. Karna
"Sensitivity Of Boron Nitride Nanotubes Toward Biomolecules Of Different Polarities."

J. Phys. Chem. C 114, 4149 (2010)
H. He, R. Pandey, I. Boustani and S. P. Karna
"Metal-like Electrical Conductance in Boron Fullerenes"

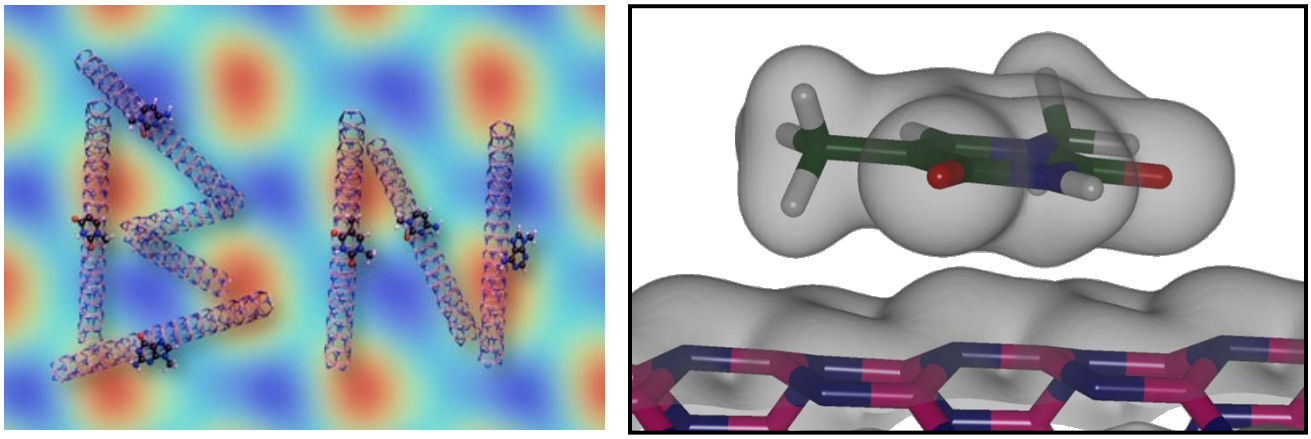
J. Phys. Chem. Lett. 1, 1584 (2010)
X. Zhong, R. Pandey, A. R. Rocha, and S. P. Karna
"Can Single-Atom Change Affect Electron Transport Properties of Molecular Nanostructures such as C_{60} Fullerene?"

Nanotechnology, 21, 165703 (2010)
S. Mukhopadhyay, S. Gowtham, R. H. Scheicher, R. Pandey, S. P. Karna
"Theoretical Study Of Physisorption Of Nucleobases On Boron Nitride Nanotubes: A New Class Of Hybrid Nano–biomaterials."

(http://iopscience.iop.org/0957-4484/labtalk-article/42205)

New nano-bio hybrid material unveiled :

Interfacing biomolecules – often referred to as "soft" matter – with the generally "hard" materials of nanotechnology, and ensuring that the former retain their remarkable properties, requires control of both the nature and spatial distribution of the molecular interactions that take place between the two. The potential application of the unique signature of these materials in probing the structural and conformational changes of biological systems may possibly lead to new detection mechanisms.



DNA/RNA nucleobases on BNNTs

Comparing the results with an earlier study performed by group, the scientists conclude that interaction of nucleobases with BNNT/CNT is dominated mainly by the van der Waals forces, with a slender contribution from Coulombic forces in the case of nucleobase conjugated BNNT.

Useful characteristics

The higher binding energy of the guanine–BNNT conjugate and the associated smaller band gap relative to that of the pristine BNNT could potentially be useful characteristics for device makers looking for a mechanism to distinguish guanine from the other nucleobases.

More details can be found in the journal *Nanotechnology*.